

BEHAVIOR OF MINERAL MATTER DURING ALKALINE LEACHING OF COAL

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Introduction

A process for producing premium quality coal with a very low ash content was demonstrated recently (1). This process involves reacting the material with a hot alkaline solution to dissolve quartz and to convert clay minerals and iron pyrite into acid-soluble compounds which are removed in a second step by treatment with acid. To understand this process better, several minerals which generally make up a major portion of the ash-forming mineral matter in many coals were reacted individually with hot alkaline solutions, and the solid reaction products were characterized by X-ray diffraction (XRD). In this study, quartz, kaolinite, and iron pyrite were reacted individually with Na_2CO_3 , NaHCO_3 , and NaOH solutions using various concentrations and temperatures. The solid products were identified and their solubility in dilute mineral acids demonstrated. In addition, the extent of conversion of quartz and pyrite to acid-soluble species was demonstrated for various alkaline treatment conditions.

Experimental Methods

The materials used for this study, obtained from sources listed in Table 1, were checked for impurities by XRD. Using this method, no impurities were detected in the quartz, but the kaolin appeared to contain a significant amount of quartz and trace quantities of illite and titania. The iron pyrite was obtained as nodules by handpicking the refuse produced in cleaning coal from Mahaska County, Iowa. The nodules were crushed and ball-milled to $-38\ \mu\text{m}$ size. Part of the ground pyrite was treated for 1 hr. with excess 1.2 M HCl at 70°C under a nitrogen atmosphere (to remove acid-soluble impurities) and then washed and dried. This acid-cleaned material contained about 88% FeS_2 , based on total sulfur content, and significant amounts of quartz and kaolinite plus a trace of titania. In addition, it seemed to contain some amorphous material which may have been coal. The raw pyrite which had not been treated with acid contained all of these impurities plus significant amounts of calcite and iron oxides.

Table 1. Materials which were leached

Material	Source	Impurities
Quartz	Ottawa sand (Ill.)	None
Kaolin	Old Hickory No. 5 ball clay (Ky.)	SiO_2 , Illite, TiO_2
Raw pyrite	Coal, Mahaska County (Ia.)	CaCO_3 , iron oxides SiO_2 , kaolinite, TiO_2
Cleaned pyrite	Same as above	SiO_2 , kaolinite, TiO_2

For the leaching experiments, a weighed amount of finely divided mineral matter was mixed with 120 ml. of alkaline solution in a 300 ml. stainless steel autoclave equipped with a turbine agitator. The system was flushed with nitrogen and then heated to the desired leaching temperature. A nitrogen overpressure of 3.4 atm. was maintained throughout the leaching process. The mixture was stirred continuously while leaching was conducted at constant temperature and pressure for a specified period. After this treatment, the autoclave was cooled quickly, and the contents of the autoclave were filtered to recover any undissolved solids. The solids were washed with water, dried in an oven, weighed, and divided into two parts. One portion was analyzed by XRD with a Siemens D500 diffractometer using copper K α radiation. The other portion was usually subjected to an acid treatment and washing step in order to determine the proportion of acid-soluble material.

For the acid treatment step, up to 3 g. of alkali-leached material was mixed with 300 ml. of mineral acid (approximately 2.0 M) in a stirred, three-neck Pyrex reaction flask for 30 min. The treatment was conducted either at room temperature (25°C) or at the boiling point (100°C). After the treatment the mixture was filtered, and any undissolved solids were washed with water, dried, weighed, and analyzed by XRD.

Experimental Results

In one set of experiments, -38 μ m size quartz particles were leached with various hot alkaline solutions to study the effects of alkali type, alkali concentration, ratio of alkali to quartz, temperature, and leaching time on dissolution. After each leaching, the reactor contents were filtered with Whatman No. 40 filter paper using suction, and the residue was washed with cold water, dried at 350°C for 2 hr., and weighed. The percentage of material extracted was calculated using the following expression:

$$\text{Extraction (\%)} = 100 - \frac{\text{wt. of residue}}{\text{wt. of feed}} \times 100 \quad 1)$$

The results of leaching quartz with Na₂CO₃ solutions having different concentrations are shown in Figure 1. For each point, 2.0 g. of quartz was leached with 120 ml. of solution at 250°C for the indicated time. It can be seen that the amount of material extracted increased linearly with time for about the first hour. During this period the rate of extraction also increased with alkali concentration to approximately the 0.5 power. Following the constant rate period, the extraction stopped. Apparently the solubility limit was reached, and it seemed to be the solubility limit at room temperature rather than at the leaching temperature. The following evidence pointed to the lower temperature limit. The residue remaining after leaching quartz for 2 hr. or more was an amorphous, non-crystalline solid which was insoluble in hot HCl. The results suggested that quartz had dissolved in the hot solution, and upon cooling some of the silica and possibly some of the soda had reprecipitated as an amorphous or glassy material. On the other hand, the residue remaining after quartz had been leached for less than 1 hr. appeared to be largely quartz. Furthermore when quartz was leached for 1 hr. at 300°C with a 1.0 M solution, the amount of material extracted was only 69% which was no greater than the maximum amount extracted at 250°C. From published solubility data (2) for silica in various alkaline solutions, one would expect the solubility of quartz in a Na₂CO₃ solution to increase markedly with temperature.

Even though the amount of silica extracted seemed to be limited by the room temperature solubility limit, this limit was raised by increasing either the alkali concentration or the ratio of alkali to quartz. Thus by increasing the alkali concentration from 1.0 M to 2.0 M, the maximum amount extracted was raised from 70% to 98.5%. Moreover when the quantity of quartz leached in 1 hr. with a 1.0 M solution at 250°C was reduced from 1 g. to 2 g., the percentage extracted increased from 58% to 95%.

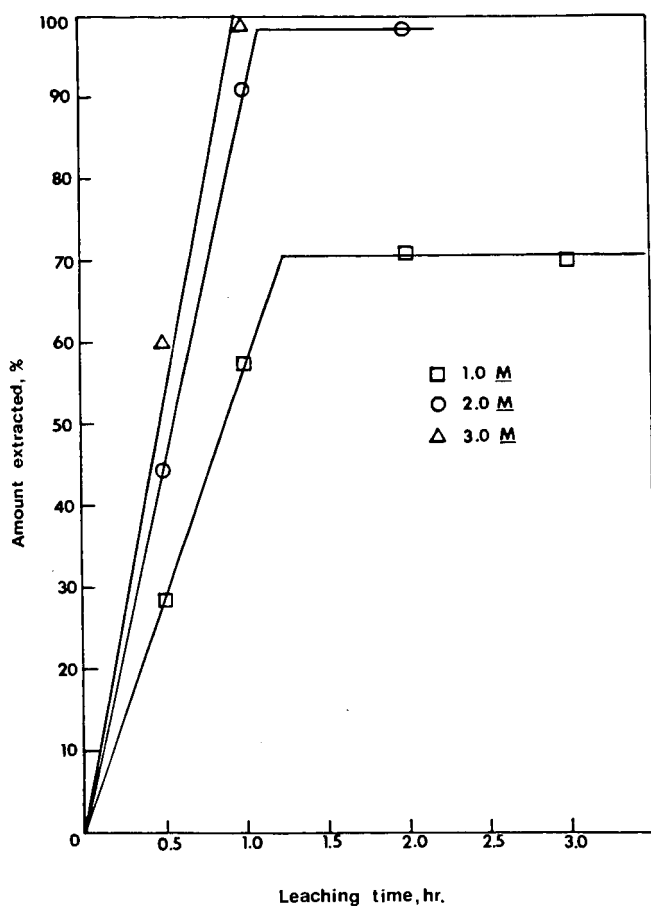


Figure 1. Dissolution of quartz (2.0 g.) by hot (250°C) sodium carbonate solutions (120 ml.) having different concentrations (1.0-3.0 M).

Quartz was also leached for 1 hr. at 250°C with either 2.0 M NaOH or NaHCO₃. In each case 2.0 g. of quartz was leached with 120 ml. of solution. Most of the quartz (99.5%) was converted to soluble sodium silicates and extracted by the hot caustic. On the other hand, only 10% of the quartz was extracted by the NaHCO₃ solution, and the residue appeared to be entirely quartz. These values were noticeably different from the 58% extracted by 1.0 M Na₂CO₃ under similar conditions. Therefore, these leachants were not equivalent even though each provided the same number of moles of sodium.

None of the residues remaining after leaching quartz with any of the alkalis were acid-soluble.

In a second set of experiments, -74 μm size kaolin particles were leached with hot alkaline solutions to study the conversion of kaolinite to various sodium hydro-aluminosilicate compounds (Table 2) under different leaching conditions. In each experiment, 15 g. of kaolin was leached with 120 ml. of alkaline solution. The solid reaction product was recovered by filtration, washed with water, dried in an oven at 95°C, and analyzed by XRD. Although this method of analysis identified the minerals present, it provided only an approximate indication of the relative proportions of the various minerals present. Quartz was particularly misleading because the method of detection was very sensitive to this mineral. Therefore, the results are reported only in terms of major, minor, and trace quantities present in the product as indicated by XRD (Table 3). Because the small amount of titania in the kaolin was apparently not affected by even the most rigorous leaching conditions, the product always contained a trace of this material so no further mention seems necessary.

When kaolin was leached with 1.0 M Na₂CO₃ at 200°C for 1 hr., most of the kaolinite was converted to the sodalite-type natrodavayne (NS) while the quartz and illite impurities were not affected noticeably (Table 3). Increasing the leaching temperature to 250°C resulted in the conversion of the kaolinite to a mixture of mixed-type natrodavayne (NCS) and analcime (A) and complete dissolution of the quartz impurity. The illite impurity was not affected. Leaching at 300°C and above resulted in the conversion of the kaolinite to the cancrinite-type natrodavayne (NC). Only at 350°C did the illite impurity appear to be affected.

A similar trend was observed when kaolin was leached for 1 hr. at 250°C with Na₂CO₃ solutions of different concentrations (Table 3). At the lowest concentration (0.2 M), part of the kaolinite was converted to the sodalite-type natrodavayne while the impurities were untouched. At the highest concentration (2.0 M), the kaolinite was converted to the cancrinite-type natrodavayne, and although the quartz was extracted, the illite remained.

Somewhat similar changes were observed when the leaching time was varied while holding the concentration of Na₂CO₃ at 1.0 M and the temperature at 250°C. With a leaching time of 0.5 hr. the kaolinite was converted to a mixture of analcime and sodalite-type natrodavayne, whereas with a leaching time of 2.0 hr. the kaolinite was largely converted to the cancrinite-type natrodavayne. Not all of the quartz was extracted when leaching was conducted for 0.5 hr., but all of the quartz appeared to be removed when leaching was conducted for longer periods. However, the illite remained even after 2 hr. of leaching.

When kaolin was leached with 1.0 M NaOH at 250°C for 1 hr., most of the kaolinite appeared to be converted to analcime (Table 3). Increasing the concentration to 2.0 M resulted in converting most of the kaolinite to hydroxycancrinite (HC). In either case the quartz impurity was extracted but the illite impurity remained.

Leaching kaolin with 2.0 M NaHCO₃ at 250°C for 1 hr. converted the kaolinite to the sodalite-type natrodavayne, but it had no apparent effect on the impurities.

Table 2. Various sodium hydroaluminosilicates produced in leaching kaolinite with hot alkaline solutions

Mineral	Chemical formula	Symbol
Analcime	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4(\text{SiO}_2) \cdot 2(\text{H}_2\text{O})$	A
Hydroxycancrinite	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2(\text{SiO}_2) \cdot \frac{2}{3}(\text{NaOH}) \cdot n(\text{H}_2\text{O})$	HC
Hydroxysodalite	(same as above)	HS
Natrodavynne (sodalite-type)	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2(\text{SiO}_2) \cdot \frac{1}{3}(\text{Na}_2\text{CO}_3) \cdot n(\text{H}_2\text{O})$	NS
Natrodavynne (cancrinite-type)	(same as above)	NC
Natrodavynne (mixed type)	(same as above)	NCS

Table 3. Results of leaching 15 g. kaolin (-74 μm) with 120 ml. alkaline solution

Leaching conditions				Mineral products excluding TiO_2 , type, (amount) ^a
Alkali	Conc., M	Temp., °C	Time, hr.	
Na_2CO_3	1.0	200	1.0	NS(maj), SiO_2 (maj), kaolinite(min), illite(tr)
Na_2CO_3	1.0	250	1.0	NCS(maj), A(maj), illite(tr)
Na_2CO_3	1.0	300	1.0	NC(maj), A(min), illite(tr)
Na_2CO_3	1.0	350	1.0	NC(maj)
Na_2CO_3	0.2	250	1.0	SiO_2 (maj), kaolinite(min), NS(min), illite(tr)
Na_2CO_3	0.5	250	1.0	SiO_2 (maj), NS(maj), illite(tr)
Na_2CO_3	1.0	250	1.0	NCS(maj), A(maj), illite(tr)
Na_2CO_3	2.0	250	1.0	NC(maj), illite(tr)
Na_2CO_3	1.0	250	0.5	A(maj), NS(maj), SiO_2 (min), illite(tr)
Na_2CO_3	1.0	250	1.0	NCS(maj), A(maj), illite(tr)
Na_2CO_3	1.0	250	2.0	NC(maj), A(min), illite(tr)
NaOH	1.0	250	1.0	A(maj), HS(min), illite(tr)
NaOH	2.0	250	1.0	HC(maj), A(min), illite(tr)
NaHCO_3	2.0	250	1.0	NS(maj), SiO_2 (maj), illite(tr)

^a Amount: maj = major quantity, min = minor quantity, tr = trace quantity.

To investigate the dissolution of the sodium hydroaluminosilicates produced by alkaline leaching, 3.0 g. portions of the leached product were treated with 300 ml. of acid in a stirred flask for 30 min. Either 2.0 M HCl or 1.8 M H_2SO_4 were utilized. While HCl was always used at the boiling point, H_2SO_4 was sometimes used at the boiling point and sometimes at room temperature. From XRD analysis of the solid residue remaining after the acid treatment, it was found that all of the sodalite-type and cancrinite-type compounds were dissolved by the acids whether hot or cold. On the other hand, analcime was completely dissolved only by the boiling acids.

In a third set of experiments, $-38\ \mu\text{m}$ pyrite particles were leached with hot alkaline solutions to study the conversion of iron pyrite to iron oxide and soluble sulfur species. In each experiment, 5 g. of acid-cleaned pyrite was leached with 120 ml. of alkaline solution for 1 hr. In addition to analyzing the solid residue by XRD, the total sulfur content of the leachate was determined in order to estimate pyrite conversion.

When iron pyrite was leached for 1 hr. with 1.0 M Na_2CO_3 at 250°C , only 12.7% of the pyrite was converted to iron oxide and soluble sulfur species (Table 4). Increasing the leaching temperature to 300°C raised the conversion to 26.4%, and increasing the temperature to 350°C raised the conversion to 44.8%. In each case the solid residue consisted principally of hematite and unreacted pyrite.

Increasing the Na_2CO_3 concentration, while maintaining the leaching time at 1 hr. and temperature at 250°C , increased the pyrite conversion only slightly (Table 4). On the other hand, when pyrite was leached with 2.0 M NaOH at 300°C for 1 hr., a conversion of 62% was achieved. Again, hematite appeared to be the principal solid reaction product.

When the pyrite residue from the alkaline leaching step was treated with acid, all of the hematite dissolved in either hot HCl or H_2SO_4 . However, the hematite appeared to dissolve incompletely or very slowly in cold H_2SO_4 . Unreacted pyrite was not touched by the acid whether hot or cold.

Conclusions

The solubilization of several of the most prevalent minerals in coal was demonstrated by a one- or two-step treatment process. The first step involves treatment with a hot alkaline solution while the second step involves treatment with a dilute mineral acid.

It was shown that fine-size quartz particles readily dissolve in 1-2 M Na_2CO_3 or NaOH at 250°C . However, when quartz is extracted by a hot Na_2CO_3 solution which is then cooled, an amorphous, acid-insoluble material is produced under some conditions. A likely possibility is that amorphous silica precipitates when the room temperature solubility limit of the material is exceeded. Formation of the amorphous material is prevented by using higher concentrations of alkali or a higher ratio of alkali to silica.

It was also shown that kaolinite reacts with hot alkaline solutions to form various sodium hydroaluminosilicates which are acid-soluble. The particular sodium hydroaluminosilicate formed depends on the type of alkali employed, the alkali concentration, the treatment temperature, and length of treatment. When Na_2CO_3 is employed, kaolinite is largely converted to the sodalite-type natrodavne under less rigorous conditions and to the cancrinite-type natrodavne under more rigorous conditions. Under intermediate treatment conditions, the mixed-type natrodavne and analcime are produced. When NaOH is employed, kaolinite is largely converted to analcime and hydroxycancrinite with the latter being favored by higher alkali concentrations.

Table 4. Results of leaching 5 g. acid-cleaned pyrite ($\sim 38 \mu\text{m}$) with 120 ml. alkaline solution for 1 hr.

Alkali	Leaching conditions		Conv., %	Residue
	Conc., M	Temp., °C		
Na_2CO_3	1.0	250	12.7	$\text{FeS}_2, \text{Fe}_2\text{O}_3$
Na_2CO_3	1.0	300	26.4	$\text{FeS}_2, \text{Fe}_2\text{O}_3$
Na_2CO_3	1.0	350	44.8	$\text{FeS}_2, \text{Fe}_2\text{O}_3$
Na_2CO_3	1.0	250	12.7	$\text{FeS}_2, \text{Fe}_2\text{O}_3$
Na_2CO_3	2.0	250	14.5	----
Na_2CO_3	3.0	250	15.8	----
NaOH	2.0	300	62.0	$\text{FeS}_2, \text{Fe}_2\text{O}_3$

It was further shown that iron pyrite reacts with hot alkaline solutions to form hematite and soluble sulfur species. NaOH is considerably more effective than Na_2CO_3 for this reaction. However, the effectiveness of Na_2CO_3 solutions can be increased by increasing the treatment temperature and to a lesser extent by increasing the alkali concentration. The hematite produced is readily dissolved by hot mineral acids.

Work is in progress to extend the described reactions to other minerals associated with coal. Further studies are also directed to leaching of coal itself. The results will be used to relate the behavior of the individual minerals when leached alone to their behavior when leached together in their natural occurrence with coal. The studies will shed light on the potential of demineralizing coal for use in low-ash, low-sulfur coal-water mixtures as fuel for replacing oil.

Literature Cited

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